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(54) DETERGENT COMPOSITIONS

(57) A detergent composition containing (a) one or more surfactants, (b) at least 5% by weight of an alkali metal carbonate, and (c) 5—30% by weight of an acid which forms water-soluble calcium salts and magnesium salts and/or calcium complexes and magnesium complexes having a pK_1 value of 2.8—4.8, in which (b) and (c) are separate, component (c) having a higher rate of solubility in a wash liquor than the alkaline component which is present in excess, component (c) dissolving so that the wash liquor has a pH of 2.0 to 5.0 before its temperature reaches 25°C., any alkaline material hardly dissolving before the temperature of the wash liquor reaches 40°C, and dissolving before the wash liquor reaches 60°C, and imparting a pH of from 9.0 to 10.5. The compositions may be put up in sachets.

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FIG.1

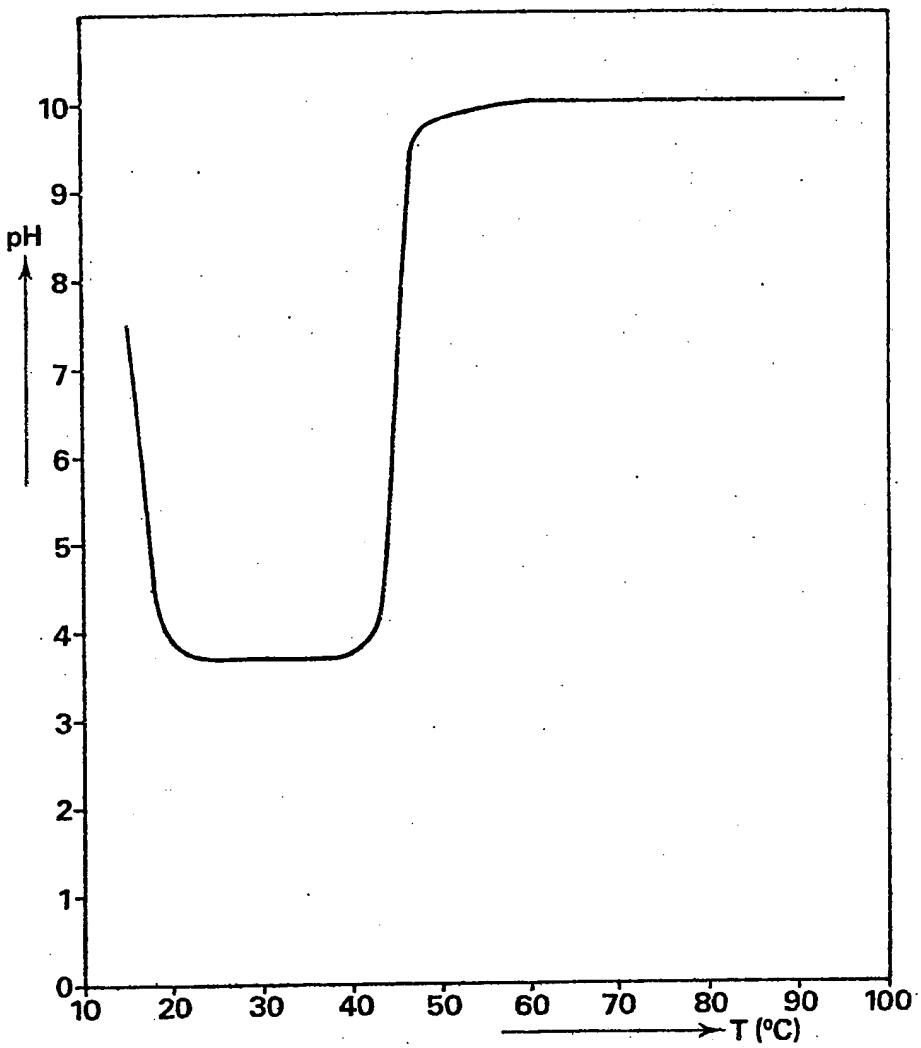

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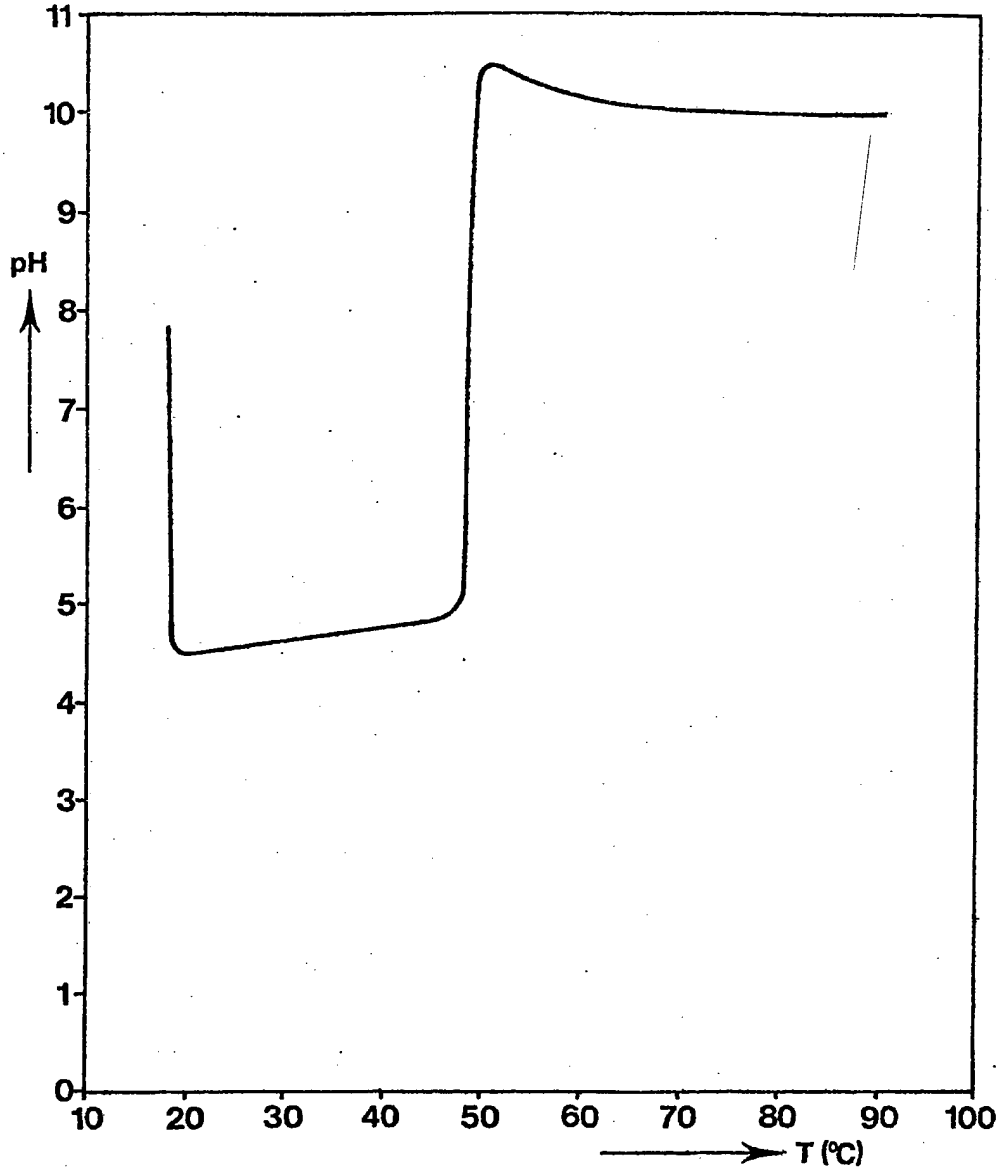
FIG.2



SPECIFICATION

DETERGENT COMPOSITIONS

The present invention relates to a detergent composition containing one or more surfactants, an alkali metal carbonate, and an acid which forms water-soluble calcium salts and magnesium salts and/or calcium complexes and magnesium complexes, and in which detergent composition the acidic constituent and the alkaline constituent are separately present, the acidic constituent having a higher rate of solubility in a wash liquor than the alkaline constituent, and the total amount of alkali being present in excess relative to the amount of acid. A detergent composition of this type is described in United States Patent Specification No. 3 761 415.

This patent specification describes a phosphate-free detergent composition consisting of citrates, such as citric acid, an alkali metal carbonate, and a synthetic surfactant. The citrate ions go into solution before the alkali metal carbonate and dissolve to such an extent that the formation of water-insoluble calcium and magnesium carbonates is inhibited. The composition described in the above-mentioned patent specification possesses the disadvantage, however, that a relatively high weight percentage of citrates needs to be incorporated therein to prevent the above-mentioned precipitation. At a German Hardness of 6° the wash liquor preferably contains 0:5 percent by weight of citric acid and 1:0 percent by weight of the alkali metal carbonate. The detergent compositions given in the examples contain 33 to 57 percent by weight of citric acid converted for an integrated product.

For reasons of economy, partly because of the relatively high cost price of citrates and citric acid, such a percentage is unacceptably high. Moreover, even at low initial hardness values the remaining hardness appears to be relatively high, which for example unfavourably affects the envisaged cleaning effect. The detergent compositions of the present invention do not possess these drawbacks.

The present invention provides a solution to the problem of excluding from the detergent composition those components that are or may be harmful from an ecological point of view. Examples of such potentially harmful components which are frequently employed are sodium polyphosphate and other phosphates. Phosphates form an indispensable nutrient for vegetable and animal life. When present in high concentrations in stagnant or slowly flowing water, however, they may give rise to an excessive growth of algae. One of the consequences is a decrease of the oxygen content in the deeper parts of the water, and anaerobic processes may cause the formation of gases such as methane and carbon disulphide. These phenomena may have a detrimental influence on fish-stock and may cause considerable damage to areas of natural beauty and recreation.

In view of the severity of this problem in the last few years there has been an intensive search for suitable substitutes for phosphates in detergent compositions.

The phosphates are added to the detergents because they are capable, for example, of binding calcium ions and magnesium ions to form soluble complexes. As a result, these ions can no longer form unwanted precipitates with ingredients of the wash liquor or with dirt held by the fabric to be laundered. These precipitates are objectionable because they deposit on the heating element of the washing machine and on the laundered fabric. Substitutes for phosphates that have previously been proposed include oxidized polysaccharides, certain cellulose derivatives, citrates, nitrilotriacetates and water-insoluble sodium alumino-silicates. Total replacement of phosphates has so far been realized only on a limited scale.

It has now been found that the above problem can be solved in an inexpensive way by the use of a detergent composition based on an alkali metal carbonate. Conventional detergent compositions based on alkali metal carbonates suffer from the disadvantage that during successive washing cycles there is a considerable accumulation of water-insoluble carbonates on the fabric being cleansed and on the heating element of the washing machine. This drawback is further aggravated in that this incrustation is cumulative and increases more than proportionally as a function of the number of washing cycles. As a result, the quality of the fabric treated with these compositions will be affected and the fabric will display little absorption power and be stiff and hard to the touch; moreover, wear and discoloration will occur. Furthermore, as a result of ageing, the carbonate precipitate will become more and more difficult to dissolve.

The present invention provides a detergent composition containing one or more surfactants, an alkali metal carbonate, and an acid which forms water-soluble calcium salts and magnesium salts and/or calcium complexes and magnesium complexes and in which detergent composition the acidic constituent and the alkaline constituent are separately present, the acidic constituent having a higher rate of solubility in a wash liquor than the alkaline constituent, and the total amount of alkali being present in excess relative to the amount of acid, the acidic constituent comprising 5 to 30 percent by weight, based on the weight of the detergent composition, of an acid having a pK_1-value in the range of from 2.8 to 4.8 and dissolving to such an extent in the wash liquor that as the wash liquor gradually increases in temperature the said wash liquor has a pH in the range of from 2.0 to 5.0 before its temperature reaches a value of 25°C., and the alkaline constituent comprising an alkali metal carbonate in an amount of at least 5 percent by weight based on the detergent composition, and hardly dissolving before the temperature of the wash liquor reaches a value of 40°C, and practically entirely dissolving

before the wash liquor reaches a temperature of 60°C and imparting a pH to the liquid in the range of from 9.0 to 10.5.

It has been found, however, that in one washing cycle so little precipitate is formed on the heating element and so little fabric incrustation occurs that the above-mentioned drawbacks are not met. The detergent composition of the invention results in both the fabric incrustation and the deposit on the heating element formed in one washing cycle being brought into solution at the beginning of the next washing cycle by a reaction with acid under mildly acid conditions which should be maintained sufficiently long to allow the precipitated carbonates almost completely to dissolve. Subsequently, as a result of the alkaline constituent going into solution, the wash liquor is softened. The presence of the alkali metal carbonate in the water causes the calcium ions and the magnesium ions contained in the wash liquor to be precipitated as water-insoluble carbonates. For maximum softening and optimum washing effect the pH of the wash liquor, after almost complete dissolution of the alkaline constituent, should be in the range of from 9.0 to 10.5. The use of the compositions of the present invention neither leads to appreciable accumulation in a fabric of insoluble carbonates or other salts, nor to the formation of any harmful deposit on the heating elements. Moreover, only a relatively low percentage by weight of acid, based on the weight of the detergent composition is required.

It should be added that German Patent Specification No. 2 437 173 describes a process which comprises successive treatments with an acidic pre-wash detergent composition and an alkaline main-wash detergent composition based on sodium carbonate. The present invention has the advantage over the process described in German Patent Specification No. 2 437 173 in that the envisaged prevention of appreciably cumulative incrustation is realised by the use of a single detergent composition. Moreover, when use is made of the detergent composition of the invention it is unnecessary and sometimes even undesirable for the wash liquor to be entirely or substantially drained off between the acid and the alkaline phase of the washing process.

The acid contained in the acidic constituent should be capable of forming calcium salts and magnesium salts and/or complexes that are at least moderately soluble in water. The amount of acid should be sufficiently high to dissolve calcium carbonate and magnesium carbonate deposited on a heating element and in a fabric. The required percentage by weight of acid is dependent, *inter alia*, on the acid used, the bicarbonate content and the hardness of the water employed for the washing treatment.

In practice it has been found that an amount of 5 to 30 percent by weight, based on the weight of the detergent composition, is sufficient. The acidic constituent should dissolve to such an extent in the wash liquor, which gradually increases in temperature, that the wash liquor has a pH in the range of from 2.0 to 5.0 before its temperature reaches 25°C. If the pH drops to below 2.0, then certain types of fibres may be damaged. On the other hand, a pH above 5.0 would result in practice in the carbonate taking too long to dissolve completely.

The pK_1-value of the acid should be in the range of 2.8 to 4.8. If the acid has a pK_1-value below 2.8, then the pH of the wash liquor may temporarily drop to below 2.0, whereas a pK_1-value above 4.8 would call in practice for the use of uneconomically large amounts of acid in order to attain a pH below 5.0.

The acidic constituent should also have the above-mentioned properties in order that the mildly acid conditions may be maintained sufficiently long for the precipitated carbonates to dissolve completely.

Examples of acids which have these properties are adipic acid, succinic acid, citric acid, diglycolic acid, lactic acid, tartaric acid, glycolic acid and fumaric.

The acidic constituent may, of course, also contain a mixture of acids. Preferably, the acid constituent is then a mixture of adipic acid, glutaric acid and succinic acid. It has been found that such a mixture dissolves very rapidly and moreover influences very favourably the rate of solubility of the precipitated carbonates during the acid phase of the washing process.

If the acidic constituent contains a mixture of acids, then at least one acid should have a pK_1-value in the range of from 2.8 to 4.8.

Such an acid may be mixed with inorganic acids such as sodium bisulphate. In combination with other acids use may also be made of polycarboxylic acids, such as polyacrylic acid, the acid forms of oxidized cellulose and starch mono- and polycarboxylated products obtained by substitution of the hydrogen atoms of starch and cellulose such as carboxymethyl cellulose and dicarboxymethyl starch.

One or more conventional components may be incorporated into the acidic constituent depending on the envisaged application of the detergent composition. Preferably, the acidic constituent contains a surfactant. Its presence results in the acids, the washing and the precipitated carbonates being wetted more rapidly, which favourably influences the rate of solubility of the carbonates. Ethoxylated fatty alcohols are particularly suitable for this purpose.

Another category of materials that may be incorporated into the acidic constituent are pre-compounds such as peroxides, which have an optimum bleaching effect at a pH lower than that at which the detergent composition displays optimum cleaning action.

Compounds such as peroxomonosulphate, which have insufficient storage stability in conventional detergent compositions, may also be included in the acidic constituent.

After the acidic constituent has dissolved, the pH of the wash liquor may, during the acid phase of

the washing process, rise to a maximum value of 6.5 to 7.0. This increase in pH is caused by the gradual dissolution of the precipitated carbonates. The value to which the pH rises is dependent upon bicarbonate content and the hardness of the tap water, the amount of washing, the fabric incrustation and the degree of precipitation on the heating element.

The alkaline constituent should contain an amount of alkali such that after the alkaline constituent has almost completely dissolved the pH of the wash liquor is from 9.0 to 10.5. This pH is required to obtain an optimum cleaning effect and effective softening. Preferably, the alkali used is an alkali metal carbonate or a mixture of an alkali metal carbonate and, for example, sodium silicate.

The alkali content may vary between wide limits. The detergent composition should however contain at least 5 percent by weight of alkali metal carbonate in order that the calcium ions and the magnesium ions may be precipitated in the wash liquor. A lower percentage would be ineffective under the most favourable conditions. In some circumstances it may be desirable for the detergent composition to contain as much as 65 percent by weight of the alkali metal carbonate.

A suitable alkali metal carbonate is sodium carbonate. Sodium carbonate and its hydrates, however, are relatively sensitive to moisture. With the present detergent compositions this may lead to difficulties since this detergent composition contains an acidic as well as an alkaline constituent. The rather high alkalinity sometimes is also a drawback. For these reasons, in addition to calcined sodium carbonate the alkaline constituent may contain as the alkali metal carbonate, sodium bicarbonate and/or sodium sesquicarbonate. These combinations of compounds are less sensitive to moisture than sodium carbonate and its hydrates, and also have a lower alkalinity.

Furthermore, the alkaline constituent may contain one or more usual detergent components such as surfactants, builders, bleaching agents, fluorescent brighteners, enzymes, foaming agents, substances such as sodium carboxymethyl cellulose, which serve to prevent dirt from re-depositing on the fabric, bactericides, corrosion inhibitors, perfumes, and/or colourants.

Surfactants which may be used are the water-soluble salts of higher fatty acids ("soaps") or the synthetic surfactants described in, for example Netherlands Patent Specifications Nos. 7 403 381 and 7 406 306.

Preferably the surfactant contained in the alkaline constituent should be an alkyl ether sulphate. Alkyl ether sulphate have the advantage that they contribute to reducing incrustation. Preferably sodium tall fatty alcohol ether sulphate is used. The alkaline constituent hardly dissolves until the temperature of the wash liquor reaches a value of 40°C and it goes practically completely into solution before the temperature reaches 60°C.

The alkaline constituent should have this property in order that on the one hand the mildly acid conditions may be maintained for a sufficiently long time and on the other hand the pH of the wash liquor may be brought to 9.0 to 10.5 before the washing temperature of 60°C is reached. The dissolution of the alkaline constituent may be retarded in various ways.

For example, known shaping techniques, which are grouped here under the generic name of agglomeration techniques, may be used. By agglomeration techniques are meant, *inter alia*, pelletizing, tabletting, granulating, extruding, marumerizing, briquetting or rolling followed by cutting. In this way also the surface area of the alkaline constituent is drastically reduced, which is, of course, of importance in the present invention. The most important parameters influencing the rate of solution are the composition of the alkaline constituent, the shaping method and the shaping pressure, if required.

Preferably, the alkaline constituent is provided with a coating which practically does not disintegrate before the temperature of the wash liquor reaches a value of 40°C and practically entirely disintegrates before the temperature reaches 60°C.

By disintegration is meant, *inter alia*, dissolution and dispersion. The amount of coating material used is 0.1 to 15, and preferably 0.5 to 10 percent by weight, based on the weight of the detergent composition. The coating material may be any material generally employed for this purpose.

Examples of suitable water-soluble or water-dispersable polymers are polyethylene glycols, polyvinyl alcohols, polyvinyl pyrrolidone, polyvinyl acetate, carboxymethyl cellulose, carboxymethyl starch, hydroxypropyl cellulose, gelatin, or gum arabic, provided that they are applied in a sensible manner. Particularly preferred are (co)polymers of methacrylic acid and methacrylic esters, available under the trade names Eudragit L 30 D and E 30 D.

Another specific embodiment of the invention comprises coating the alkaline constituent with higher fatty acids which melt at a temperature in the range of from 35° to 50°C., much as lauric acid. As the temperature increases during washing, these compounds will melt and react with the alkali metal carbonate to form water-soluble salts exhibiting washing action. The acidic and the alkaline constituent should be separately present in the detergent composition. It is only necessary, however, that the two constituents can be separately distinguished. This requirement consequently does not exclude the two constituents from being in contact with each other. The acidic constituent in the form of a powder may be directly mixed with the alkaline constituent. However, it may also be agglomerated just as the alkaline constituent. The detergent composition according to the invention may also be obtained by entirely or partly providing the coated alkaline constituent with a coating of the acidic constituent. In this way, separation of the constituents of the detergents composition during storage is prevented.

Preferably the detergent composition is in the form of a feed unit comprising a sachet entirely or

partly made of a material permeable to or disintegrating in water and filled with the acidic and the alkaline constituent. In this way the acid is prevented from contacting the washing before it dissolves. As a result, even the slightest chance of fibre damage is avoided.

Such a sachet may consist of a material which does not disintegrate in water and which is closed with a strip of material which does disintegrate in water. Alternatively, the sachet may be closed by seams joined with a material that disintegrates in water.

Examples of suitable materials that do not disintegrate in water are polyethylene, polypropylene and polyvinyl chloride. To close the sachet a water dispersible paper may be used. Preferably, however, the sachet consists entirely or partly of a non-woven material. This material is permeable to water and relatively strong.

A sachet is filled with an amount of detergent composition which is sufficient for one washing cycle. The filled sachet can therefore be added to wash the liquor. Preferably, the detergent composition should be in the form such that there is no direct contact between the acidic and the alkaline constituent.

To achieve this a sachet of the type described above may be filled with an acidic and an alkaline constituent, the latter constituent being provided with a coating which practically does not disintegrate before the temperature of the wash liquor reaches a value of 40°C and practically entirely disintegrates before the temperature reaches 60°C. It is preferred that feed units of the detergents composition should be in the form such that the sachet has two compartments, the acidic constituent being contained in the one and the alkaline constituent in the other compartment.

Such a feed unit comprises for example a sachet consisting of 2 non-woven outer walls and a polyethylene partition, the one compartment being filled with a powdered acidic constituent and the other compartment with a coated alkaline constituent. The seams of these sachets may be sealed with a glue or by using pressure at elevated temperatures.

Alternatively, the sachets may be formed so that the alkaline constituent goes into retarded dissolution as a result of the construction of the sachet.

The use of such sachets has the advantage that the alkaline constituent may be contained in the sachet in the form of a powder. A sachet may thus be made in which the compartment containing the alkaline constituent (the "alkaline" compartment) entirely or partly consists of a material which becomes permeable to water or disintegrates at a temperature in the range of from 40° to 60°C. The term "disintegration" as used here includes tearing of the sachet. A sachet may in principle consist of, for example, 3 layers of material, the outer wall of the "acid" compartment being permeable to water, the outer wall of the alkaline constituent being impermeable to water and the partition wall for example consisting of a mixture of poly(meth)acrylic acid (Eudragit L 30 D) and hydroxypropyl methyl cellulose. A partition wall thus composed will tear at a temperature in the range of from 40°C to 60°C, after which the alkaline constituent can freely dissolve in the wash liquor.

The water-permeable outer wall preferably consists of a non-woven material. Various materials may be used for the water-impermeable wall. Preferably however polyethylene, polypropylene, polyvinyl chloride or a non-woven material provided with a water-insoluble coating is used. Alternatively, the "alkaline" compartment may be closed with a strip which is permeable to water or which disintegrates at a temperature in the range of from 40°C to 60°C. Such a strip may be provided as a connecting strip between an impermeable partition wall and outer wall. Such a strip may for example entirely or partly consist of polyvinyl alcohol or a mixture of poly(meth)acrylic acid (Eudragit L 30 D) and hydroxypropyl methyl cellulose. Preferably, however, the alkaline compartment should be provided with one or more seams that open in water at a temperature in the range of from 40 to 60°C. A sachet of this type may be made by providing in the seams a material which disintegrates at a temperature in the range of from 40° to 60°C. The seams may then be entirely or partly formed by a mixture of polyethylene glycol and one or more thermoplastic acrylic resins. Polyethylene glycol having a molecular weight of 1500 melts at a wash liquor temperature of 42°C, after which the seams will open.

The following Examples serve to further describe the present invention.

EXAMPLE I (Comparative).

The following experiment was carried out in a Zanker washing machine (EA 5A). The volume of the wash liquor was 16 litres. The water had a German Hardness of 15°, and a bicarbonate content of 200 mg/litre. 216 grams of the integrated detergent composition as described in Example VIII of United States Patent Specification No. 3 761 415 were added to the washing liquor. The composition consisted of 35 percent by weight of citric acid, 63.5 percent by weight of sodium carbonate and 1.5 percent by weight of a synthetic detergent.

The relationship between time, temperature and degree of acidity of the wash liquor was measured.

After two minutes at a temperature of 20°C. the wash liquor had a degree of acidity of 8.7. After 10 minutes at 37°C the pH value was 8.9 and after 40 minutes at 87°C it was 9.25.

As a result of the relatively high citrate ions concentration and the low pH hardly any calcium carbonate or magnesium carbonate was precipitated. The above data show that both theoretically and in practice this detergent composition differs from the compositions of the present invention.

Whereas the object of the above-mentioned patent specification is to prevent the precipitation of

calcium carbonate and magnesium carbonate, the present invention envisages the very formation of such a precipitate.

Accordingly, the detergent compositions of the present invention contain a much smaller percentage by weight of acid. The characteristic of the citrate ions going into solution before the sodium carbonate, as described in the United States Patent Specification, is necessary and adequate since complexing takes place practically instantaneously.

Although for the present invention it is also desirable that the acidic constituent should go into solution before the alkaline constituent, this characteristic is in itself inadequate. The present invention can only be realized if the detergent composition has the required rate of solubility. This requirement therefore forms an essential element of the present invention.

EXAMPLE II.

The following experiments were carried out in a Zanker washing machine (EA 5A). In each experiment the amount of dirty washing was 4 kg and the wash liquor volume 16 litres.

The German Hardness of the water was 15° and bicarbonate content 200 mg/l. Table I mentions a number of detergent compositions. Compositions I and II are conventional detergent compositions based on alkali metal carbonates.

Compositions III and IV are detergent compositions of the invention. The alkaline constituents of compositions III and IV were obtained by mixing, extruding and marumerizing the components. The alkaline constituent of product III was treated with an aqueous dispersion of Eudragit L 30 D, a copolymer of methacrylic acid and the alkaline constituent of product IV with an aqueous dispersion of Euragit E 30 D, a polymer of methacrylic esters. The amounts of the detergent compositions added to the wash liquor were 150, 110, 170 and 145 grams, respectively.

The relationship between temperature and pH of the wash liquor was measured for composition III. Figure 1 shows this relationship. The results of the washing experiments showed that the primary washing action, i.e. the removal of dirt and stains by the respective compositions III and IV was significantly better than for the conventional detergent compositions I and II. Table II records the deposit on the element and the incrustation after washing 24 cycles. Compared to the conventional detergent compositions based on alkali metal carbonates it can be seen that the use of the detergent compositions of the invention resulted in hardly any accumulation of insoluble carbonates on the heating elements or in the special test fabrics.

EXAMPLE III.

The following experiment was carried out under the conditions described in Example II.

Special test fabrics were washed to determine the degree of incrustation. A feed unit in accordance with the invention comprised a non-woven sachet 12 x 23 cm having only one compartment which was filled with 205 grams of a detergent composition comprising the ingredients listed in Table I (product V).

The fumaric acid was present as a powder. The alkaline constituent was obtained by pelletizing. These pellets, which had a diameter of about 5 mm, were then coated with lauric acid. During the washing cycle the relationship between the pH and the temperature of the wash liquor was determined. Table III shows this relationship.

After the same material had been washed 10 times, the incrustation was 0.30%, after 20 washings it had been increased to only 0.42%. After 20 washings the deposit on the heating element was as little as 0.15 grams. The above experiment confirms the results described in Example II.

EXAMPLE IV.

The following experiments were carried out in a Miele automatic washing machine (number 416). Special test fabrics were washed to determine the degree of incrustation. The water had a German Hardness of 15°, and a bicarbonate content of 200 mg/l. A feed unit according to the invention comprised a 2-compartment sachet 14 x 16 cm having an outer wall of a laminated non-woven material for the "alkaline" compartment and an outer wall of a non-woven material for the "acid" compartment and a partition wall of polyvinyl chloride film. A connecting strip was provided on one side of the sachet between the outer wall of the "alkaline" compartment and the partition wall. This strip was about 0.05 mm thick and tore at a temperature of between 45° and 60°C. This strip consisted of a mixture of 15 parts of Eudragit L 30 D (30% by weight) and 2 parts of Methocel HG 4000 (hydroxypropyl methyl cellulose).

The seams of the sachet were sealed with glue. The acidic constituent comprised:

25 grams of fumaric acid
4 grams of tallow fatty alcohol, 25 ethylene oxide.

The alkaline constituent comprised:

52.7 grams of anhydrous sodium carbonate
42.4 grams of sodium perborate
11.9 grams of sodium disilicate
4.0 grams of sodium palmitate
9.0 grams of lauryl ether sulphate

1.0 grams of carboxymethyl cellulose
0.5 grams of optical brightener
0.6 grams of sodium salt of ethylene diamine-tetra-acetic acid
0.5 grams of silicone oil

After 15 washing cycles, in which the same test fabrics were always washed, it was found that the primary cleaning effect of the detergent composition of the invention was not inferior to that of phosphate-containing detergent compositions. After 4, 7 and 15 washing cycles the incrustation values were 0.21, 0.25 and 0.49 percent, respectively. These values show that in this respect the present detergent composition is not inferior in quality to the conventional phosphate-containing detergent compositions.

EXAMPLE V.

The following washing experiments were conducted in an Erres washing machine (AEG 341). In each case the amount of washing was 3.5 kg. The water had a German Hardness of 15°. A feed unit according to the invention comprised a 2-compartment sachet 13 x 15 cm having an outer wall of a polyethylene laminated non-woven material for the "alkaline" compartment, an outer wall of a non-woven material dusted with polyethylene for the "acid" compartment and a polyethylene partition wall. The 4 seams between the water-permeable outer wall and the partition wall were permanently sealed. 2 of the 4 seams between the outer wall of the "alkaline" compartment and the partition wall were permanently sealed. The two other seams were filled with a material which disintegrated in water between 40° and 50°C. This material consisted of a mixture of 10 percent by weight of polyethylene glycol having a molecular weight of 1500 and 90 percent by weight of a mixture of thermoplastic acrylic resins.

The seams were sealed by applying pressure at an elevated temperature. The polyethylene glycol melts at 42°C. As the seams opened, the alkaline constituent was released into the wash liquor. The acidic constituent was present in the form of extrudates about 0.8 mm in diameter and 1 to 3 mm long. The alkaline constituent was present in the form of powder. The acidic constituent comprised of:
6.9 grams of adipic acid
6.9 grams of succinic acid
9.2 grams of glutaric acid
2.7 grams of tallow-fatty alcohol, 25 ethylene oxide.
The alkaline constituent comprised:
8.0 grams of tallow-fatty ether sulphate
5.7 grams of sodium dodecyl-benzene sulphonate
2.0 grams of the sodium salt of hardened rape seed oil
10.0 grams of sodium disilicate
38.0 grams of sodium perborate
48.0 grams of anhydrous sodium carbonate
1.0 grams of carboxymethyl cellulose.

In a bundle test, a cotton material was washed 17 times with the above-mentioned detergent composition at a temperature of 90°C. The relationship between the temperature and the pH of the wash liquor in the 17th washing cycle is shown in Figure 2.

The primary cleaning effect compares with that of conventional phosphate-containing detergent compositions.

After the material had been washed 5, 11 and 17 times, the incrustation values were 0.30, 0.42 and 0.59 percent, respectively.

The above results clearly demonstrate the effect and the favourable results that may be obtained with the detergent composition according to the invention.

TABLE I

Components	Detergent composition (% by weight)				
	I	II	III	IV	V
sodium palmitate	8,0	10,9	7,1	8,3	8,3
tallow fatty alcohol-25-ethylene oxide	2,5	3,5	2,2	2,6	–
sodium dodecyl benzene sulphonate	5,3	7,3	4,7	5,5	5,9
Sikalon D 1)	9,3	21,8	8,3	30,3	6,7
sodium perborate	26,7	36,4	23,5	27,6	19,0
sodium salt of ethylene diamine-tetra-acetic acid	0,4	0,5	0,4	0,4	0,3
sodium carboxymethyl cellulose	0,7	0,9	0,6	0,7	0,4
optical brightener	0,4	0,5	0,4	0,4	0,3
calcined sodium carbonate	16,7	–	26,6	6,9	33,2
sodium bicarbonate (0 aq)	23,3	9,1	8,8	–	–
water	6,7	9,1	5,9	6,9	4,2
Eudragit L 30 D	–	–	4,1	–	–
Eudragit E 30 D	–	–	–	1,8	–
fumaric acid (powdered)	–	–	7,4	8,6	19,5
lauric acid	–	–	–	–	7,3

1) Sikalon D (trade name): 88% sodium disilicate + 12% H_2O

TABLE II

Detergent composition	deposit on element (in g)	fabric incrustation (in % by weight)
I	6,3	4,9
II	5,1	3,2
III	0,2	0,2
IV	0,1	0,1
V	0,2	0,1
VI	0,2	0,1

TABLE III

Temperature (°C)	pH
25	3,1
30	3,1
37	3,1
41	3,3
45	4,3
49	7,4
53	9,4
90	9,7

CLAIMS

1. A detergent composition containing one or more surfactants, an alkali metal carbonate, and an acid which forms water-soluble calcium salts and magnesium salts and/or calcium complexes and magnesium complexes and in which detergent composition the acidic constituent and the alkaline constituent are separately present, the acidic constituent having a higher rate of solubility in a wash liquor than the alkaline constituent, and the total amount of alkali being present in excess relative to the amount of acid, the acidic constituent comprising 5 to 30 percent by weight, based on the weight of the detergent composition, of an acid having a pK_1-value in the range of from 2.8 to 4.8 and dissolving to such an extent in the wash liquor that as the wash liquor gradually increases in temperature the said wash liquor has a pH in the range of from 2.0 to 5.0 before its temperature reaches a value of 25°C., and the alkaline constituent comprising an alkali metal carbonate in an amount of at least 5 percent by weight based on the detergent composition, and hardly dissolving before the temperature of the wash liquor reaches a value of 40°C, and practically entirely dissolving before the wash liquor reaches a temperature of 60°C and imparting a pH to the liquid in the range of from 9.0 to 10.5.

2. A detergent composition as claimed in claim 1 wherein the acidic constituent contains adipic, succinic, citric, diglycolic, lactic, tartaric acid, glycolic acid or fumaric acid.

3. A detergent composition as claimed in claim 1 wherein the acidic constituent contains a mixture of adipic acid, glutaric acid and succinic acid.

4. A detergent composition as claimed in claim 1 or claim 2 wherein the acidic constituent contains a surfactant.

5. A detergent composition as claimed in any one of the preceding claims wherein the alkaline constituent contains an alkyl ether sulphate.

6. A detergent composition as claimed in any one of the preceding claims wherein the alkaline constituent is provided with a coating which does not significantly disintegrate before the temperature of the wash liquor reaches 40°C and practically entirely disintegrates before the temperature reaches 60°C.

7. A detergent composition as claimed in claim 6 wherein the coatings comprises from 0.5 to 10 percent by weight based on the weight of the detergent.

8. A feed unit of the detergent composition as claimed in any one of the preceding claims which unit comprises a sachet which consists entirely or partly of a material which is permeable to or disintegrates in water and which is filled with the acidic and the alkaline constituent.

9. A feed unit as claimed in claim 8 wherein the sachet consists entirely or partly of a non-woven material.

10. A feed unit as claimed in claim 8 or claim 9 wherein the sachet has 2 compartments, the acidic constituent being contained in the one compartment and the alkaline constituent in the other compartment.

11. A feed unit as claimed in claim 10 wherein the compartment containing the alkaline constituent consists partly or entirely of a material which becomes permeable to water or disintegrates in water at a temperature in the range of from 40° to 60°C.

12. A feed unit as claimed in claim 11 wherein the compartment containing the alkaline constituent is provided with one or more seams which open in water at a temperature in the range of from 40° to 60°C.

13. A feed unit as claimed in claim 12 wherein the seams are composed entirely or partly of a mixture of polyethylene glycol and one or more thermoplastic acrylic resins.

14. A detergent composition as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples II to V.

15. A feed unit as claimed in claim 8 substantially as hereinbefore described with reference to Examples IV or Example V.

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